

The effect of silane coupling agent on the sliding wear behavior of nanometer ZrO₂/bismaleimide composites

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Abstract The polymer composites filled with nanoparticles have good friction and wear properties and widely used in many fields. The performances of nanocomposites are influenced extensively by the nanoparticles morphology, size, volume fraction and dispersion. Nanometer ZrO₂ particles have good properties, lower prices and shows good foreground in resist-materials of polymer composites. In this paper, the nanometer ZrO₂ particles are treated by silane coupling agent of N-(2-aminoethyl)- γ -aminopropylmethyl dimethoxy silane. The effect of nanometer ZrO₂ content and silane coupling agent on the friction and wear properties of BMI copposites filled with nanometer ZrO₂ are investigated. The composites filled with untreated ZrO₂ and treated ZrO₂ are prepared by the same way of mechanical high shear dispersion process and casting method. The sliding wear performance of the nanocomposites is studied on an M-200 friction and wear tester. The experimental results indicate that the frictional coefficient and the wear rate of the composites can be reduced by filled with nanometer ZrO₂. The composites containing treated nanometer ZrO₂ have the better tribological performance than that containing untreated nanometer ZrO₂. The results are explained from the SEM morphologies of the worn surface of matrix resin and

the composites containing nanometer ZrO₂ and the TEM photographs of the nanometer ZrO₂ dispersion in the matrix.

Introduction

Nanoparticles have been widely used as fillers to improve the tribological performance of polymeric composites, such as nano-ZrO₂/polyetheretherketone (PEEK) [1, 2], nano-Al₂O₃/polyphenylene sulfide (PPS) [3], nano-ZnO/polytetrafluoroethylene (PTFE) [4], nano-TiO₂/epoxy [5], nano-Al₂O₃/polyimide [6], nano-SiO₂/PEEK [7], nano-SiC/PEEK [8, 9]. Especially, nano-Si₃N₄ has shown superiority which can be oxidized into SiO₂ during the friction process to improve the characteristics of transfer film, result in reducing the friction coefficient and increasing wear resistance of polymer composites [10–12]. Besides, the synergistic effects of nano-Al₂O₃ and micro-CaSiO₃ in increasing wear resistance of epoxy resin [13] and the different pretreatments of nanoparticles effecting on tribological performance of polymer composites are also investigated [14]. Compared to the composites filled with micrometer particles, one of the distinct advantages of the composites filled with nanometer particles lies in that the performance improvement is often acquired at relatively low concentration of the nano-fillers. This is beneficial to the mechanical properties, processability and aesthetic appearance of the end-products. Certainly, the performance of the composites filled with nanoparticles is influenced extensively by the filler morphology, size, volume fraction and dispersion.

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Silane coupling agents are often applied to improve the adhesion of the matrix resin to the reinforcement particles [15]. Recently, Liang et al. [16] studied the friction and wear properties of potassium titanate whiskers reinforced bismaleimide (BMI) composites and the surfaces of whiskers treated by silane coupling agents and titanate coupling agents, respectively. The results showed that the wear-resistance of the matrix improved by the incorporation of whiskers into the matrix, while the composite containing silane coupling agent treated whiskers had the best wear-resistance.

BMI resin is the unique combination of high service temperature, good toughness and epoxy-like processing. Especially curing BMI with O,O'-diallyl bisphenol A results in the formation of a high-performance thermoset resin [17] and is widely used in some of the most important applications ranging from military programs to electronic engineering [18]. Now, there are many reports on BMI resin modification for improving its toughness. However, There are a few reports on the tribology performances of BMI resin only limiting investigation of the erosion wear properties of the material. In the early years, Mathias [19], Brandstadter [20] and Karasek [21] subsequently investigated the erosion behavior of a graphite-fiber-reinforced BMI composite with angular aluminum oxide erodent impacting to the compositions surface, the results suggested that the erosion rate of the composite is dominated by the brittle graphite fibers, resulting in erosion rates of composites much higher than those of the matrix polymer. The results imply that BMI resin has good tribology properties by nature. In our previous works, we reported the sliding wear performance of nanometer Si₃N₄-filled BMI compositions [22] and nanometer SiC-filled BMI compositions [23]. In this paper, we studied the effect of nanometer ZrO₂ content and silane coupling agent on the friction and wear properties of BMI composites filled with nanometer ZrO₂.

Experimental

Raw materials

The nanometer ZrO₂ particles were obtained from Hebei East Nanometer Materials Ltd. Co., China. Its diameter is about 20–40 nm. The coupling agent N-(2-aminoethyl)- γ -aminopropylmethyldimethoxy silane (JH-53) was supplied by Jingzhou Jiangnan Fine Chemical Co. Ltd., China. 4,4'-Bismaleimidodiphenylmethane (BMI) was obtained from Hubei

Fenggang Chemicals, China. O,O'-Diallylbisphenol A (DABPA) was obtained from Sichuan Jiangyou Material, China. All the materials involved in this work are industrial grades and used as received without any further purification. The chemical structures of BMI and DABPA as well as JH-53 were represented in Fig. 1.

Preparation of the composites of BMI filled with nanometer ZrO₂

The BMI composites filled with nanometer ZrO₂ were made by the casting method. Firstly, nanometer ZrO₂ was ultrasonically dispersed in acetone for about 10 min. Both BMI and DABPA were heated at 120 °C for 15 min under vigorous stirring to form a clear homogeneous prepolymer. Then the fillers with desired proportion were carefully mixed with the prepolymer by a mechanical high shear dispersion process. The mixture consisting of prepolymer, the nano-filler and acetone was heated to 120 °C in an oil bath and kept at this temperature for 30 min with stirring to evaporate acetone. Finally, the compounds were poured into a preheated mold with release agent, and evacuated for additional 30 min at 120 °C to remove air bubbles. All the samples were cured following the procedures: 150 °C for 2 h, 180 °C for

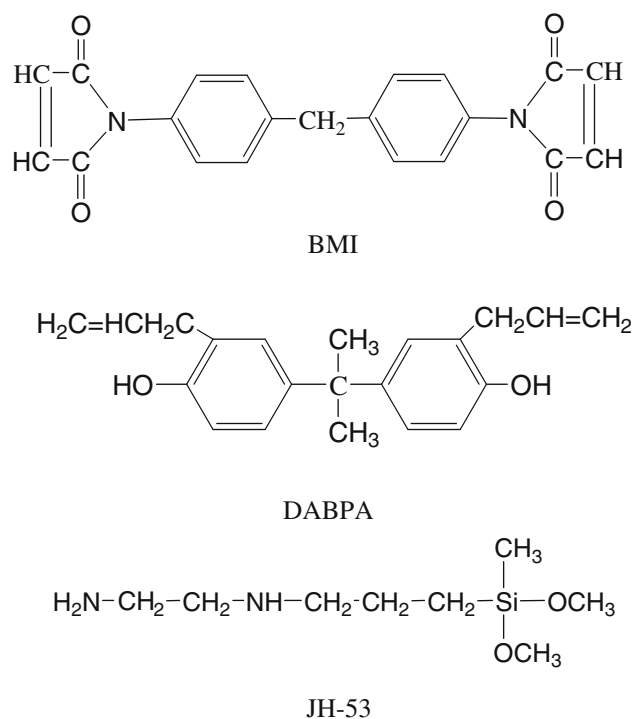


Fig. 1 Chemical formulae of BMI, DABPA and JH-53

2 h, 220 °C for 4 h. A post-curing process of the samples took place at 250 °C for 6 h.

The BMI composites filled with treated nanometer ZrO_2 were prepared in the same method as the BMI composites filled with untreated besides the nanometer ZrO_2 need to modify by silane coupling agent JH-53 before used. A solution containing 1.0 g coupling agent of JH-53 in acetone with some water, and desired proportion nanometer ZrO_2 were added into a flask. Under vigorous stirring, this suspension was ultrasonicated at room temperature for 20 min, and heated at 76 °C for 1 h. After centrifugation, washing with ethanol and drying in vacuum at 50 °C, the coupling agent modified nanometer ZrO_2 were obtained.

Measurement of the properties of materials

The mechanical properties of pure BMI resin and the composites were carried out by Chinese Standard methods. Three-point bending tests of the composites specimens were carried out in a ZMGI-250 tester in accordance with GB/T2570-1995 standard at a deformation rate of 5 mm/min, while unnotched impact tests were conducted in a XCJ-40 tester according to GB/T2571-1995 standard. Hardness of materials was measured according to HG2-168-65 under a loading of 62.5 kg and the steel ball with diameter 5 mm.

The sliding wear properties were conducted on a M-200 model friction and wear tester according to reference [7]. Sliding was performed under ambient conditions over a period of 2 h at a sliding speed of 0.42 m s^{-1} and under a load of 196 N. Before each test, the plain carbon steel ring and the matrix resin or its composite block was abraded with No. 600 abrasive paper, and then the steel ring was cleaned with cotton dipped in alcohol, and the composite blocks were also cleaned in alcohol and dried at 110 °C for 2 h to remove the alcohol and moisture and then cooled in a vacuum dry device to ambient temperature, providing for the initial weight measurement and friction test. At the end of each test, the blocks were cleaned and dried in the same way for the wear weight loss measurement. The density of the matrix and the filled composites samples was measured by Archimedes principle using absolute alcohol as the immersing medium. This mass loss could accurately be measured by determining the weight of the specimen before and after the experiment. A characteristic value, which described the wear performance under the chosen conditions for a tribosystem, was the specific wear rate ω , which was calculated from the relationship

$$\omega = \frac{\Delta m}{\rho F_N L} \left(\frac{\text{mm}^3}{\text{Nm}} \right)$$

where Δm was the worn specimen mass (g), ρ was the density of the composites (kg/m^3), F_N was the normal force (N) and L was the sliding distance (m).

The morphologies of the worn surfaces and wear debris were observed using the AMRAY-1000 B model scanning electron microscope (SEM). The distribution of nanometer ZrO_2 in matrix resin was verified with a transmission electron microscope (TEM) after the rod of the composite was sliced up into super thin sheet by microtome.

Results and discussion

The effect of nanometer ZrO_2 content on the sliding wear properties of composites

Figure 2 shows the friction coefficient as a function of the friction time for the matrix and the composites containing different proportion untreated nanometer ZrO_2 . It can be seen that the friction coefficient of all samples attained to a steady-going value in a short time after about 20 min in process of the friction test, and the frictional coefficient decreases with the increase of the mass fraction of nanometer ZrO_2 . This is to say, the higher the proportion of nanometer ZrO_2 , the lower the steady frictional coefficient. For example, the frictional coefficient of the bulk matrix was 0.36. While, the frictional coefficient of the composites

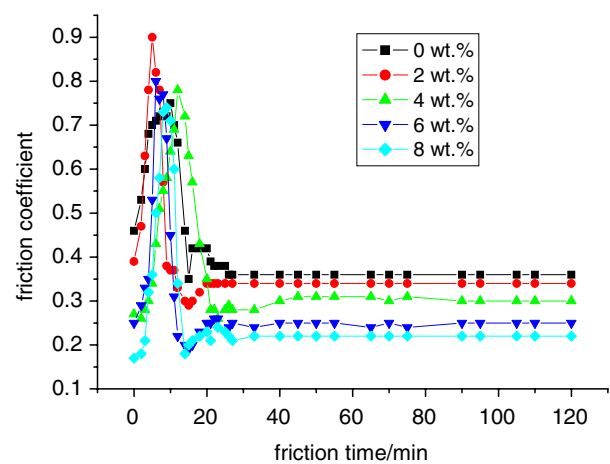


Fig. 2 Friction coefficient as a function of the friction time for the matrix and the composites containing different proportion untreated nanometer ZrO_2 (load: 196 N; sliding velocity: 0.42 m s^{-1})

containing untreated nanometer ZrO_2 was reduced from 0.34 to 0.22 when nanometer ZrO_2 content increased from 2.0 to 8.0 wt.%.

Figure 3 shows the specific wear rate of the composites filled with various amounts of nanometer ZrO_2 . It can be seen that the wear resistance of the composites are improved by the filling of the nanometer ZrO_2 under ambient dry conditions. The composites filled with nanometer ZrO_2 exhibit a considerably decreased specific wear rate in comparison with the unfilled BMI matrix. The specific wear rate of the composites is also decreased with the increase of the proportion of nanometer ZrO_2 . The specific wear rate of the composites come to the lowest value of $2.0 \times 10^{-6} \text{ mm}^3/\text{N m}$ when the proportion of nanometer ZrO_2 was 6.0 wt.%. The specific wear rate of the composites is slightly increased and come to the value of $2.1 \times 10^{-6} \text{ mm}^3/\text{N m}$ when the proportion of nanometer ZrO_2 was 8.0 wt.%. It should be noted that earlier studies [7, 22, 23] have also shown that wear resistance decreased when nanoparticles proportion exceeds the optimum value. As a matter, we found it was not possible to prepare good samples with nanometer ZrO_2 above 8.0 wt% because the system including resin prepolymer and nanometer ZrO_2 so viscous that it could not be pure into the moulding mold.

In order to understand the effect of the nanometer ZrO_2 on the friction and wear behavior of the composites, we studied the worn surfaces of the bulk matrix and the composites containing different content nanometer ZrO_2 by SEM.

Figure 4 shows the SEM photographs of the worn surface of the neat matrix and the composites containing different content untreated nanometer ZrO_2 . It can

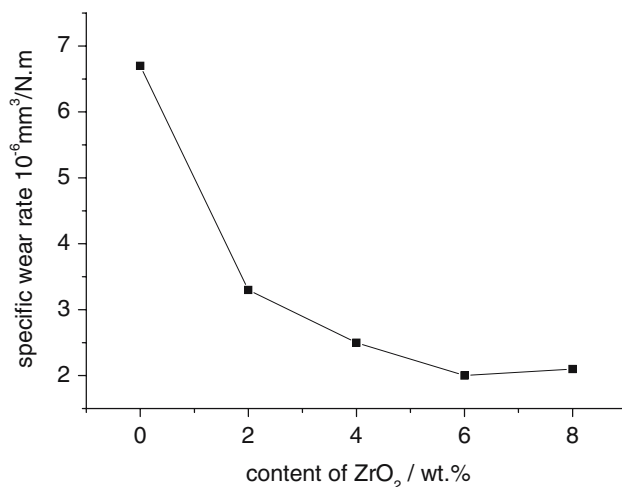
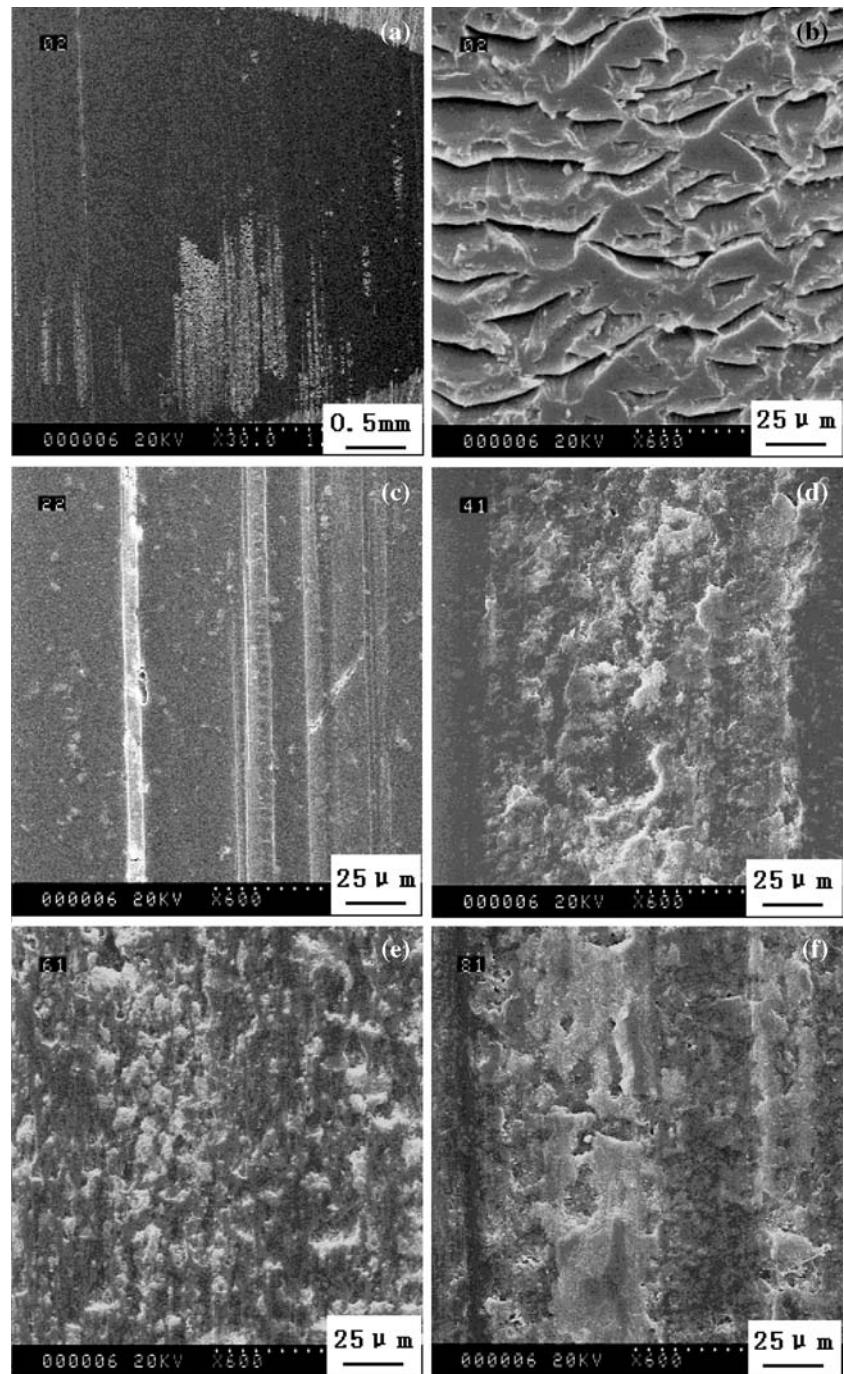


Fig. 3 Effect of the content of nanometer ZrO_2 on specific wear rate of the composites (load: 196 N; sliding velocity: 0.42 m s^{-1})

be seen that the obvious triangular shape holes in the worn surface of the neat matrix block (see Fig. 4a, b). This is indicative for fatigue-delamination generated under repeated loading during sliding. Fatigue wear has been regarded as a main mechanism responsible for the sliding of BMI resin against a hard counterpart. The model is based on the sub-surface crack nucleation and coalescence due to shear deformation of the softer surface induced by the traction of the harder asperities. This is, for the neat matrix, the fatigue-crack is the main wear mechanism. In contrast, the worn surface of the composites containing nanometer ZrO_2 appeared to be completely different. It can be seen that the slightly plucked and ploughed marks show on the worn surface of the composites containing 2.0 wt.% nanometer ZrO_2 (see Fig. 4c). While, just like same ablations on the other worn surface of the composites containing nanometer ZrO_2 from 4.0 to 8.0 wt.% are visible (see Fig. 3 from (b) to (f)) resulting from possibly the plastic flow of the resin matrix due to the high temperature during the sliding process. In particular, for the composites containing 6.0 wt.% nanometer ZrO_2 , the ablation dots were little and uniform. This implied that nanometer ZrO_2 could change the wear mechanism of BMI materials. In addition to, we notice by the magnifier that the wear debris of the neat matrix and the composites containing nanometer ZrO_2 are differently generated during sliding against the steel. The wear debris of the resin matrix is flake-like while the wear debris of the composites is tiny particulate. Especially, the wear debris of the composites containing 6.0 wt.% nanometer ZrO_2 is the tiniest. The tiny particulate wear debris is readily compacted and formed a continuous transfer film on the counterpart ring surface during sliding process in compared with flake-like wear debris. Once the stability of the transfer film on the sliding surfaces is formed, a stable friction level and low wear rates can be maintained as long as the transfer film is not destroyed. Certainly, the formation and stability of the transfer film depend upon the cohesive bond strength of the transfer film itself as well as the adhesive bond strength between the film and the sliding surfaces [24]. With the abrading function of nanometer ZrO_2 distributed in the composites, the transfer becomes thin, uniform and tenacious. As a result, the friction reduction and the wear resistance improvement of the composites containing nanometer ZrO_2 6.0 wt.% are compared with that of the resin matrix. This is in good agreement with the comments mentioned above.

In order to more find the influence factor of tribological properties, the mechanical properties and hardness of the composites are studied. Table 1 shows

Fig. 4 SEM photographs of the worn surface of the matrix and the composites containing untreated different content nanoparticles ZrO_2 : (a) neat matrix, amplification: 30 \times ; (b) neat matrix, amplification: 600 \times ; (c) 2.0 wt.% ZrO_2 ; (d) 4.0 wt.% ZrO_2 ; (e) 6.0 wt.% ZrO_2 ; (f) 8.0 wt.% ZrO_2



the mechanical properties and hardness of the composites containing different proportion untreated nanometer ZrO_2 . It is seen that the bending strength and impact strength of the composites are increased by the addition of nanometer ZrO_2 , the highest bending strength and impact strength being obtained at the composites containing 4.0 wt.% nanometer ZrO_2 . However, The bending strength and impact strength of the composites are decreased with increasing nanometer ZrO_2 content above 4.0 wt.%. Thus, it can be

inferred that a higher content of ZrO_2 is unfavorable for increasing the mechanical properties of the composites. On the other hand, it can also be seen that the hardness of the composite is almost unchanged with increasing ZrO_2 content. This implies that nanometer ZrO_2 may be ineffective for increasing the load-carrying capacity of the composites containing nanometer ZrO_2 . The hardness of the composites is not only one factor to determine the tribological behavior of materials. The interfacial interaction between the BMI

Table 1 Mechanical properties and hardness of the composites containing different proportion untreated nanometer ZrO₂

Nano-ZrO ₂ content/wt.%	Bending strength/MPa	Impact strength/kJ m ⁻²	Hardness/g (mm) ⁻²
0	106.2	9.6	25.38
2	112.5	12.6	27.14
4	118.2	14.1	28.37
6	115.7	13.7	28.50
8	113.3	11.8	28.85

matrix and the nanometer ZrO₂ may be also an important factor.

The effect of silane coupling agent on the sliding wear properties of composite

Silane coupling agents have been often applied to improve the adhesion between the organic matrix resin and the inorganic reinforcement particles to attain good machine properties. Recently, silane-coupling agents were found to modify the tribological properties of composites [16]. In this paper, the silane coupling agent JH-53 is used to treat nanometer ZrO₂, and the effect of the coupling agent on the tribological properties of the composites containing nanometer ZrO₂ is studied.

Figure 5 shows the friction coefficient as a function of the friction time for the composite containing untreated nanometer ZrO₂ and the composite containing treated nanometer ZrO₂ 6.0 wt.%. It can be seen that the steady friction coefficient of the composite containing treated nanometer ZrO₂ 6.0 wt.% is smaller

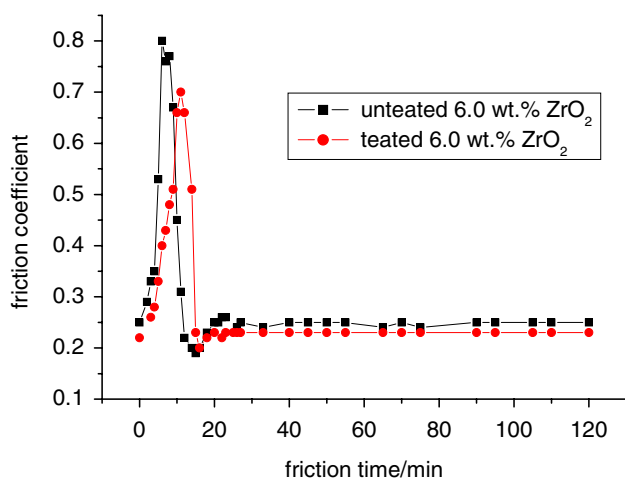


Fig. 5 Friction coefficient as a function of the friction time for the composite containing untreated 6.0 wt.% ZrO₂ and the composite containing treated 6.0 wt.% ZrO₂ (load: 196 N; sliding velocity: 0.42 m s⁻¹)

than that of the composite containing untreated nanometer ZrO₂ 6.0 wt.%, but both are not evidently different. From Table 2, it can be seen that the specific wear rate, 1.7×10^{-6} mm³/Nm, of the composite containing treated nanometer ZrO₂ 6.0 wt.% is also decreased in compared with that, 2.0×10^{-6} mm³/Nm, of the composite containing untreated nanometer ZrO₂ 6.0 wt.%. That is to say, the composites containing nanometer ZrO₂ can be exhibited better sliding wear behavior if nanometer ZrO₂ treat with the silane-coupling agent JH-53.

Figure 6 shows the SEM photographs of the worn surface of the composites containing untreated nanometer ZrO₂ 6.0 wt.% and the composites containing treated nanometer ZrO₂ 6.0 wt.% under different amplification time. Compared Fig. 6a–c, it can be seen that the worn width of the composites containing treated nanometer ZrO₂ 6.0 wt.% is more narrow than that of the composites containing untreated nanometer ZrO₂ 6.0 wt.%. Additionally, Fig. 6a shows that obvious plough-like traces have left in surface of the composites containing untreated nanometer ZrO₂ 6.0 wt.%. Some parts of the plough-like traces are marked by rectangle. Figure 6b is just the amplified parts of the rectangle in Fig. 6a. It can be seen that the composites containing untreated nanometer ZrO₂ 6.0 wt.% generate adhesive wear during the friction process. While, the worn surfaces of the composites containing treated nanometer ZrO₂ 6.0 wt.% are quite smooth can be observed (see Fig. 6d).

In order to know the reason of improvement, the dispersion of nanometer ZrO₂ in these two composites is also studied. Figure 7 shows the TEM photograph of the composites containing treated 6.0 wt.% nanometer ZrO₂ and the composites containing untreated nanometer ZrO₂ 6.0 wt.%. It can directly be seen that the treated nanometer ZrO₂ are dispersed homogeneously in resin matrix with diameter about 30 nm, while the untreated nanometer ZrO₂ are more difficultly dispersed due to the strong agglomeration tendency. Thus it can be inferred that the silane coupling agent JH-53

Table 2 Effect of the silane-coupling agent on the specific wear rate of the composite containing nanometer ZrO₂ 6.0 wt.%

Samples	Wear width/mm	Wear rate/ $\times 10^{-6}$ mm ³ (N m) ⁻¹
Neat matrix	6.14	6.7
With untreated nano-ZrO ₂ 6.0 wt.%	4.45	2.0
With treated nano-ZrO ₂ 6.0 wt.%	3.72	1.7

Fig. 6 SEM photographs of the worn surface of the composites containing untreated or treated 6.0 wt.% ZrO_2 : (a) untreated 6.0 wt.% ZrO_2 , amplification: 30 \times (b) untreated 6.0 wt.% ZrO_2 , amplification: 600 \times ; (c) treated 6.0 wt.% ZrO_2 , amplification: 30 \times ; (d) treated 6.0 wt.% ZrO_2 , amplification: 600 \times

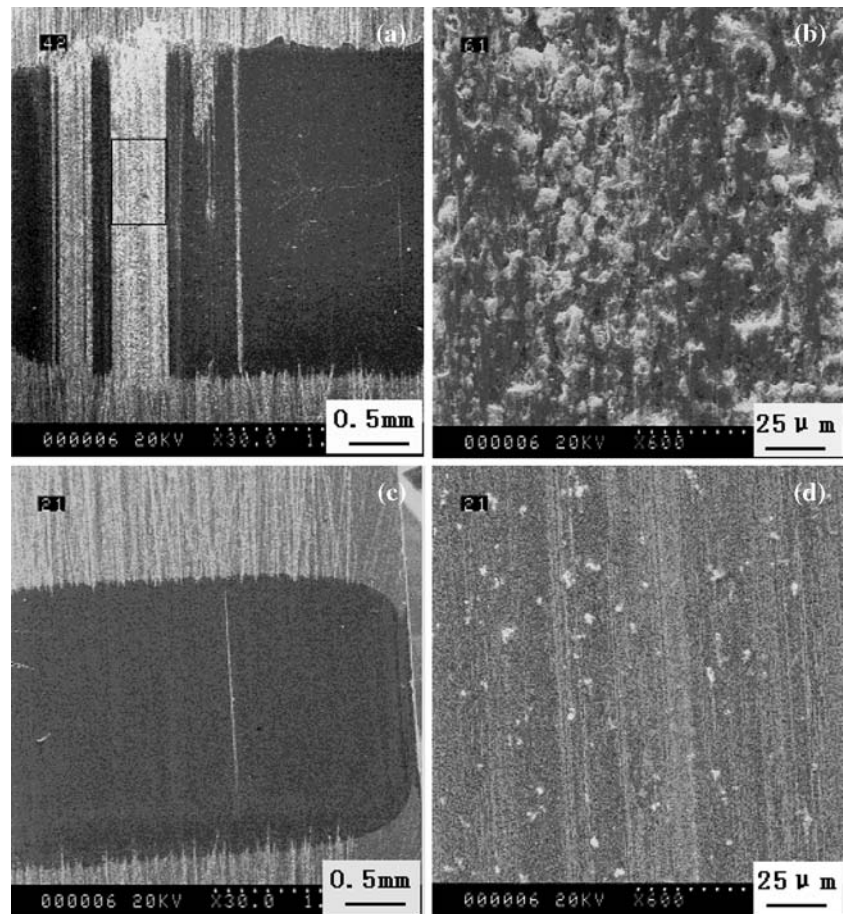
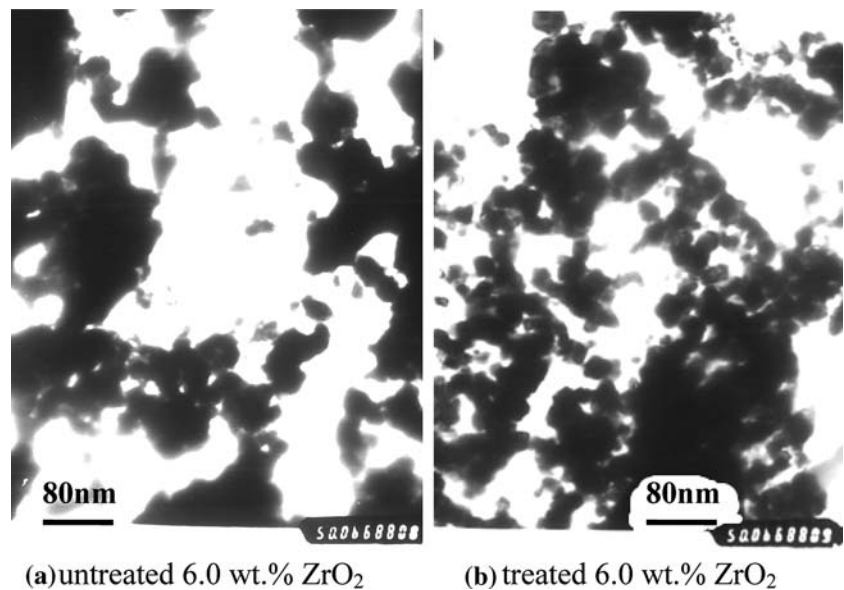


Fig. 7 TEM photograph of the composites containing untreated or treated 6.0 wt.% ZrO_2 , amplification: 50,000



improve the tribological properties of the composite containing nanometer ZrO_2 rely on the improved dispersion of nanometer ZrO_2 in matrix by the silane coupling agent JH-53.

Conclusions

From the above, the conclusions can be drawn that the friction coefficient and the specific wear rate of the

BMI resin can be decreased by filled nanometer ZrO_2 . The higher the proportion of nanometer ZrO_2 , the lower the steady frictional coefficient. The optimal content of nanometer ZrO_2 in the composite should be recommended as 6.0 wt.% for best combination of the frictional coefficient and wear rate. The severe fatigue wear of the neat resin matrix can be changed into adhesive wear and ploughed wear in the condition of the addition of nanometer ZrO_2 . The composites containing nanometer ZrO_2 will exhibit friction-reduced and wear-resisted properties if nanometer ZrO_2 can be treated with the silane-coupling agent JH-53. The reason of the silane-coupling agent JH-53 improved the tribological properties of the composites lies in the improved dispersion of nanometer ZrO_2 in matrix.

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